

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 713 357 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

22.05.1996 Bulletin 1996/21

(51) Int. Cl.⁶: **H05K 1/09, H01L 23/498**

(21) Application number: **95118153.6**

(22) Date of filing: **17.11.1995**

(84) Designated Contracting States:

DE FR GB

(30) Priority: **21.11.1994 JP 286448/94**

(71) Applicants:

- **SUMITOMO METAL CERAMICS INC.**
Yamaguchi (JP)
- **DAIKEN CHEMICAL COMPANY**
Osaka-shi, Osaka (JP)

(72) Inventors:

- **Fukuda, Junzo**
Nagoya-shi, Aichi (JP)
- **Harada, Akio**
Osaka-shi, Osaka (JP)
- **Nishigaki, Susumu**
Nakoya-shi, Aichi (JP)

(74) Representative: **Sandmair, Kurt, Dr. Dr.**

Patentanwälte
Schwabe, Sandmair, Marx
Stuntzstrasse 16
81677 München (DE)

(54) **Thick film paste**

(57) A thick film paste for use in the formation of a conductor, a resistor, an insulator, a protector or the like in a ceramic wiring substrate by a printing process, wherein at least 2-tetradecanol as a solvent is contained in an amount of at least 3% by weight. The thick film paste is excellent in printability, for example, has less viscosity change during printing and exhibits less bleeding.

EP 0 713 357 A1

Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a thick film paste which is used for the formation of a conductor, a resistor, an insulator, a protector or the like, in a ceramic wiring substrate by a screen printing process, and which is excellent in printability.

2. Description of Prior Art

A ceramic wiring substrate is produced by, for example, a process comprising screen printing a conductor paste for wiring on a fired ceramic or unfired green sheet substrate, further screen printing an insulating paste for an insulating layer thereon, drying, repeating the foregoing procedure, and firing. Beside the above conductor and insulating pastes, pastes for a resistor and a protector are applied according to necessity. These pastes are mainly used in a screen printing process, so that they are collectively called a thick film paste.

Generally, a thick film paste is prepared, for example, by adding conductive powder such as metal powder and insulating powder such as ceramic or glass powder (for the preparation of a conductor paste), or an electrically resistive component such as one based on RuO₂ (for the preparation of a resistor paste), to a mixture of an organic resin and a solvent which is called a vehicle. In the conventional vehicle, for example, ethyl cellulose or acrylic resin is used as an organic resin and butyl carbitol acetate, α -terpineol or β -terpineol is used as a solvent.

For example, U.S. Patent No. 4,394,171 (Japanese Patent Laid-Open No. 31509/1983) describes a thick film conductor composition containing a vehicle composed of ethyl cellulose (organic resin) and β -terpineol (solvent).

The conventional thick film paste using the above vehicle has a drawback in that a viscosity increase occurs during printing to thereby affect the printability. The viscosity increase would result in rendering the separation of the paste from the printing plate unsuccessful to thereby cause pinholes and, in extreme cases, cause wire breakage in the conductor and short circuit in the insulating layer. The reason for the viscosity change is that the use of an organic solvent necessitates care for ventilation and exhaust during printing and drying and the solvent is evaporated to thereby bring about an increase in the paste viscosity during printing. The conventional thick film paste has another drawback in that bleeding sometimes occurs during printing. The occurrence of bleeding in a conductor paste for wiring deteriorates fine line quality. The cause of the bleeding is poor wettability of a solvent to conductive metal powders such as Ag, Au, Pd, Pt, etc.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a thick film paste for a ceramic wiring substrate whose viscosity change and bleeding during printing are so slight as to ensure an excellent printability of the thick film paste.

The inventors have made intensive studies and, as a result, they have found that the above object can be attained by incorporating a specified compound as a solvent in a thick film paste, thereby arriving at the present invention.

That is, the present invention relates to a thick film paste which is used for the manufacture of a ceramic wiring substrate by a screen printing process and which comprises inorganic particles dispersed in a vehicle comprising an organic resin and a solvent, and, according to necessity, further includes an inorganic binder, the solvent containing 2-tetradecanol.

For the thick film paste, it is preferred that 2-tetradecanol be contained in an amount of at least 3% by weight and that the vehicle comprise 5 to 25% by weight of an organic resin and 95 to 75% by weight of a solvent.

The inorganic particles of the thick film paste are conductive powder (for a conductor paste), electrically resistive powder (for a resistor paste), insulating powder (for an insulating paste) or protector powder (for a paste for a protective layer) depending on the type of the paste, and are used in combination with an inorganic binder such as glass according to necessity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the thick film paste of the present invention, 2-tetradecanol (isotetradecanol) constituting part or the whole of the solvent has a higher boiling point, a lower evaporation rate and a less power of dissolving or swelling the green sheet than those of other solvents as apparent from Table 1. The evaporation rate given in Table 1 is a measurement obtained by putting each solvent in a vessel of 1 cm² in liquid surface area, allowing it to stand still at a test temperature for a given period of time, and determining the evaporation rate.

Table 1

Solvent	boiling point (°C)	Evaporation rate (g/cm ² · Hr)	
		80°C	100°C
2-tetradecanol	276	0.5	3.6
butyl carbitol acetate	247	2.5	7.6
α -terpineol	213	7.5	16.5

In the present invention, 2-tetradecanol as a solvent should be contained in the thick film paste in an amount of at least 3% by weight and it is preferred that the 2-tetradecanol content be at least 5% by weight. When the 2-tetradecanol content is less than 3% by weight, the object and effects of the present invention cannot be fully achieved. The whole of the solvent may be 2-tetradecanol. In this case, the balance is composed of desired inorganic particles of a conductive powder, an insulating powder or an electrically resistive powder, optionally together with an inorganic binder or the like, and a resin component. Conventionally employed butyl carbitol acetate, α -terpineol or the like can be mentioned as a solvent suitable for use in combination with 2-tetradecanol, which is, however, in no way limited thereto. Also, conventionally employed ethyl cellulose, polyvinyl butyral, acrylic resin or the like can be mentioned as the organic resin of the vehicle, which is, however, in no way limited thereto.

With respect to the proportion of the organic resin to the solvent in the vehicle, it is preferred that the organic resin and solvent contents be 5 to 25% by weight and 95 to 75% by weight, respectively, for obtaining a paste exhibiting an excellent printability. The weight ratio of the vehicle to the inorganic particles is not particularly limited and is regulated depending on the powder properties of the inorganic particles.

When the thick film paste of the present invention is a conductor paste, the conductive powder is not particularly limited. However, when the conductive powder is co-fired with green sheets, the conductive powder is varied depending on the substrate material. A high-melting metal such as molybdenum or tungsten is used as the conductive powder on a substrate material such as alumina or aluminum nitride to be fired at relatively high temperatures. On the other hand, a metal such as gold, silver, silver-palladium alloy, copper or nickel is used on a substrate material which can be fired at relatively low temperatures. The above conductive powder is mixed with glass powder according to necessity and dispersed in a vehicle to give a paste.

When the thick film paste is a resistor paste, for example, RuO_2 or an RuO_2 -based pyrochlore compound is used as an electrically resistive powder and dispersed together with glass powder in a vehicle to give a paste. When the thick film paste is an insulating paste, Al_2O_3 or Al_2O_3 with glass or crystallizable glass can be used as insulating powders. Further, when the thick film paste is a protector paste such as an overcoat paste or the like, fillers of glass, glass/ SiO_2 or Al_2O_3 can be used as inorganic particles. Whatever the paste is, it is not limited to those mentioned above and conventional materials can appropriately be utilized.

The ceramic material for use in the above ceramic substrate is not particularly limited, and alumina (Al_2O_3), aluminum nitride (AlN), silicon carbide (SiC) and various ceramics composed mainly of the above materials can be mentioned as examples thereof. Further, use can be made of a low-temperature firing ceramic in which glass powder is mixed in alumina ceramic.

The ceramic wiring substrate in which the thick film paste of the present invention is printed may have any of monolayer and multilayer structures as long as the ceramic is used as an insulator, and examples of the process for producing the multilayer ceramic wiring substrate include thick film multilayer printing and green-sheet multilayer lamination processes. Further, the circuit may be provided on only one side or both sides of the substrate.

The above two processes for producing the multilayer ceramic wiring substrate will be described. In the thick film multilayer printing process, a conductor paste and an insulating paste are alternately printed by a screen printing process on a fired ceramic substrate and fired. According to necessity, a resistor paste can be printed. An Ag- or Cu-based paste is generally used as a conductive powder.

On the other hand, in the green-sheet multilayer lamination process, first each green sheet is provided with registration-holes and through holes, and the through holes are filled with a conductor paste and a conductor paste is printed thereon. Finally, the resultant green sheets are laminated one upon another, subjected to thermocompression bonding to thereby integrate them, and fired.

The present invention will now be described in greater detail with reference to Examples and Comparative Example.

Example 1

CaO-Al₂O₃-SiO₂-B₂O₃ system glass powder and α -Al₂O₃ powder were mixed with an acrylic resin and an organic solvent such as toluene or ethanol in a ball mill and formed into ceramic green sheets each of 0.3 mm in thickness by a doctor blade method.

100 parts by weight of Ag flat powder having an average particle size of 5 μ m and a vehicle consisting of 3 parts by weight of ethyl cellulose dissolved in 17 parts by weight of 2-tetradecanol were used as printing paste materials. The above components were mixed by means of a three-roll mill to thereby give a conductor paste of a given viscosity (Example 1 in Table 2).

The above conductor paste was continuously printed at room temperature (25°C) on 1000 green sheets cut so as to have a given size by the use of a conventional screen printing machine. The viscosity of the paste was measured before and after the printing operation, thereby determining the rate of a viscosity change. In this printing, a 250-mesh screen was used and patterns of 120 μ m in width were printed. The printed face was examined as to the state of paste bleeding around the given print patterns. The results showed that the viscosity increased from 2510 P (poise) before the printing to 2660 P after the printing, exhibiting a viscosity change of +6%, and that only a very slight bleeding occurred on the printed face (Example 1 in Table 3).

Examples 2 to 5

Conductor pastes (Examples 2 and 3), a resistor paste (Example 4) and an insulating paste (Example 5) were prepared by varying the inorganic particles and inorganic binder as specified in Table 2 and also by varying the organic resin component and organic solvent constituting a vehicle as specified in Table 2, and the same experiments as in Example 1 were carried out except that the pastes of Examples 3 and 4 were respectively printed on fired 96% Al₂O₃ substrates. The printability evaluation results of each paste are given in Table 3.

Comparative Example 1

The same experiment as in Example 1 was carried out except that a conductor paste was prepared using 100 parts by weight of the Ag powder used in Example 1, 25 parts by weight of conventional butyl carbitol acetate as an organic solvent in place of the 2-tetradecanol and 4 parts by weight of ethyl cellulose. The printability evaluation results are also given in Table 3.

Table 2

Ex. No.	Inorganic particles or inorganic binder (parts by weight)	Organic resin (parts by weight)	Solvent (parts by weight)	Proportion of	
				2-tetradecanol in paste (% by weight)	organic resin in vehicle (% by weight)
1	Ag 100	ethyl cellulose 3	2-tetradecanol 17	14.2	15
2	Ag 80 Pd 20	ethyl cellulose 6	2-tetradecanol 5 butyl carbitol acetate 29	3.6	15
3	Au 95 B ₂ O ₃ -SiO ₂ -PbO system glass 5	ethyl cellulose 2	2-tetradecanol 6 butyl carbitol acetate 13	5.0	9.5

Table 2-continued

Ex. No.	Inorganic particles or inorganic binder (parts by weight)	Organic resin (parts by weight)	Solvent (parts by weight)	Proportion of	
				2-tetradecanol in paste (% by weight)	Proportion of organic resin in vehicle (% by weight)
4	RuO ₂	30	ethyl cellulose	2-tetradecanol	
			4.5	60	30.8
	CaO-Al ₂ O ₃ -SiO ₂		polyvinyl		5.3
	-B ₂ O ₃ system		butyral	α -terpineol	
	glass	70	0.5	30	
5	Cr ₂ O ₃ -CaO-Al ₂ O ₃ -SiO ₂ -B ₂ O ₃ system		ethyl cellulose	2-tetradecanol	
	glass	100	10	18	8.6
				α -terpineol	9.1
				82	
Comparative Ex. 1	Ag	100	ethyl cellulose	butyl carbitol	14
			4	acetate	25

Table 3
Evaluation of Printability

Ex. No.	Rate of viscosity change*			Max. bleeding after printing (μm)
	before printing (P)	after printing (P)	rate of change (%)	
1	2510	2660	+6	20
2	2610	2920	+12	0
3	2580	2840	+10	20
4	2360	2510	+6	30
5	1420	1600	+13	30
Comparative Ex.				
1	2200	3090	+40	80

* The rate of viscosity change was determined by measuring the viscosities before and after continuous screen printing of 1000 sheets and the mark "+" means a viscosity increase.

Rate of viscosity change (%) = [(viscosity after printing - viscosity before printing)/(viscosity before printing)] x 100

As apparent from the foregoing, the thick film paste of the present invention has an excellent printability such that the rate of viscosity change occurring when it is printed as a conductor, a resistor, an insulator, a protector, or the like, for a ceramic wiring substrate is slight and that the bleeding after printing is also slight. Consequently, the thick film paste of the present invention contributes to an efficient production of a ceramic wiring substrate with a high wiring density.

Claims

1. A thick film paste for use in the preparation of a ceramic wiring substrate by a printing process, which comprises inorganic particles dispersed in a vehicle comprising an organic resin and a solvent, optionally together with an inorganic binder, said solvent comprising 2-tetradecanol or a mixture of 2-tetradecanol and another solvent.
2. The thick film paste according to claim 1, wherein 2-tetradecanol is contained in an amount of at least 3% by weight.
3. The thick film paste according to claim 1, wherein the vehicle comprises 5 to 25% by weight of an organic resin and 95 to 75% by weight of a solvent.
4. The thick film paste according to claim 1, wherein the organic resin is ethyl cellulose, polyvinyl butyral or a mixture of ethyl cellulose and polyvinyl butyral.
5. The thick film paste according to claim 1, wherein the inorganic particles are composed of conductive powder.

EP 0 713 357 A1

6. The thick film paste according to claim 5, which contains an inorganic binder composed of glass.
7. The thick film paste according to claim 1, wherein the inorganic particles are composed of electrically resistive powder.
8. The thick film paste according to claim 7, which contains an inorganic binder composed of glass.
9. The thick film paste according to claim 1, wherein the inorganic particles are composed of insulating powder.
10. The thick film paste according to claim 1, wherein the inorganic particles are composed of protector powder.
11. The thick film paste according to claim 1, wherein the other solvent is butyl carbitol acetate or α -terpineol.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 8153

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL.6)
A	PATENT ABSTRACTS OF JAPAN vol. 3 no. 143 (E-154) ,27 November 1979 & JP-A-54 121996 (HITACHI) 21 September 1979, * abstract *	1-10	H05K1/09 H01L23/498
A	US-A-5 306 333 (DERSHEM) * column 3, line 46 - line 60 *	1,2,5,6, 11	
A	RESEARCH DISCLOSURE, no. 309, January 1990 HAVANT GB, page 41 XP 000099326 30959: 'New class of MLC (Multi Layer Ceramic) pastes' * the whole document *	1,2,5	
A	US-A-4 663 186 (INDYK ET AL.) * column 5, line 26 - line 40 *	1,3,9	
			TECHNICAL FIELDS SEARCHED (Int.CL.6)
			H05K H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 February 1996	Examiner Mes, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 150 (01.82) (P04C01)

THIS PAGE BLANK (USPTO)